Review

Catalytic oxidation of volatile organic compounds on supported noble metals

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ABSTRACT

Volatile organic compounds (VOCs) are toxic and mainly contribute to the formation of photochemical smog with a consequent remarkable impact to the air quality. A few techniques are available to reduce VOC emission, among them catalytic oxidation is suitable especially for highly diluted VOCs. The development of noble metals and transition metal oxides as catalysts for VOCs oxidation has been widely reported in the literature and the research field continues to be very active. Selection of catalytic materials for the abatement of organic pollutants is not easy because the activity depends on the specific molecule, on the reactions conditions and many parameters can affect the catalyst activity and resistance.

The present review focus on the most used noble metals catalysts for oxidation of not halogenated VOC. The effects of metal salt precursor, chlorine poisoning, water inhibition, particle size dependence, nature of the support are discussed. The calculated reaction order with respect to VOC and oxygen as well as the proposed reaction mechanisms are addressed. Examples of the most recent catalytic systems reported in literature are also included.

Contents

1. Introduction

Volatile organic compounds (VOCs) have a high vapor pressure and low water solubility and are recognized as major contributors to air pollution either, through their toxic nature and/or as precursors of ozone and photochemical smog [1,2]. VOCs are emitted from a large variety of sources, such as transport and industrial processes (outdoor sources) as well as from household products (indoor sources). Examples of industrial processes having VOCs emissions are chemical and pharmaceutical plants, petroleum refineries, automobile manufacturers, food processors, textile manufacturers, electronic component plants. Among indoor sources, office supplies, printers, insulating materials, solvents and cleaning products, pressed woods, restaurant and domestic cooking, wood stoves are recognized as major contributors to VOCs emission. The nature of VOCs depends on the process and includes alkanes, alcohols, ketones, aldehydes, aromatics, paraffins, olefins, halogenated hydrocarbons [2]. Among the most common and toxic not halogenated compounds, are worth to mention formaldehyde, benzene, carbon monoxide, toluene, propylene, phenol, acetone, styrene. Formaldehyde, causing cancer in animals and in humans, is an important chemical widely used by industry to manufacture building materials and numerous household products. Thus, it may be present in substantial concentrations both indoors and outdoors. Carbon monoxide and alkenes are among the major families of pollutants in industrial and automotive emissions; in particular propylene and toluene are recognized as highly polluting molecules because

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of their high POCP (photochemical ozone creativity potential) [3,4].

Among VOCs, halogenated and more especially chlorinated VOCs (such as dichloromethane, chloroform, carbon tetrachloride, 1,2-dichloroethane, trichloroethylene, tetrachloroethylene) have widespread applications in industry and require special attention on account of their toxicity and high stability [5].

Because of their harmful properties and due to the progressive increase of VOCs emissions, the release of VOCs into the environment is being controlled by increasingly stringent regulation. According to the Göteborg protocol, the maximum VOC emission level by 2020 in the EU member countries should be reduced by nearly half as compared to the base year 2000 [6]. Therefore, the development of new effective methods for their abatement is mandatory. The most efficient methods for VOCs destruction are thermal and catalytic incineration, the latter becoming most popular because in many cases it is more versatile and economical for low concentrations of organic emissions [7]. Moreover, the catalytic incineration operating at relatively low temperatures and in controlled conditions does not emit undesirable by-products, such as dioxins and NO_x. Selection of the catalytic materials for various organic pollutants has been the subject of many studies and the optimization of catalyst formulation does not appear an easy task, because of the large variety of organic molecules and the complicated nature of VOCs mixtures encountered in practice. Both classes of catalysts, noble metals and transition metal oxides have been widely explored for either, halogenated and not halogenated compounds [8–13]. The noble metal based catalysts, in spite of their more expensive costs, are the preferred ones because of their high specific activity, resistance to deactivation and ability to be regenerated [2]. The catalytic performances of supported noble metals strongly depend on the preparation method, type of precursor, metal loading and particle size, nature of the support [14–19]. Moreover the operating conditions used, such as VOCs and oxygen concentration, overall gas flow rate, type of reactor (fixed-bed catalytic reactor, flow-through membrane reactor) have also an important influence on the catalytic performances [20–23].

The present work would give an overview of supported Pt, Pd, Rh catalysts, as powder or supported on monolithic substrates, for catalytic combustion of model not halogenated VOC molecules in a fixed-bed catalytic reactor. The effects of metal precursor salt, metal particle size, chlorine and water poisoning are discussed. Some representative examples of the latest progress in the development of new catalytic systems are also reported.

2. Supported noble metal catalysts

2.1. Pt, Pd, Rh/Al$_2$O$_3$ catalysts: activity and application

Among the family of metallic catalysts, noble metals (Pt, Pd, Rh) supported on high-surface area γ-Al$_2$O$_3$ powder or wash-coated on a monolith are commonly used due to their high efficiency for VOC abatement [2,11,14,24–27]. The preferred catalyst substrate for industrial abatement of VOCs is a monolithic or honeycomb material, either ceramic (cordierite) or metallic (aluminum or stainless steel) with usually 200–400 channels per square inch (cpsi), where the active phase (usually Pt/γ-Al$_2$O$_3$) is deposited. Such structure offers the major advantage of low-pressure drop and is widely preferred to more traditional pellet-shaped or powder catalysts. The latter ones are used for laboratory purpose only. Moreover, it is worth to mention that recently metallic structured short-channel Cr–Al steel substrates of various geometries have been proposed as an alternative to ceramic monolith for VOCs combustion [28,29]. Such systems are able to overcome the drawbacks of monoliths
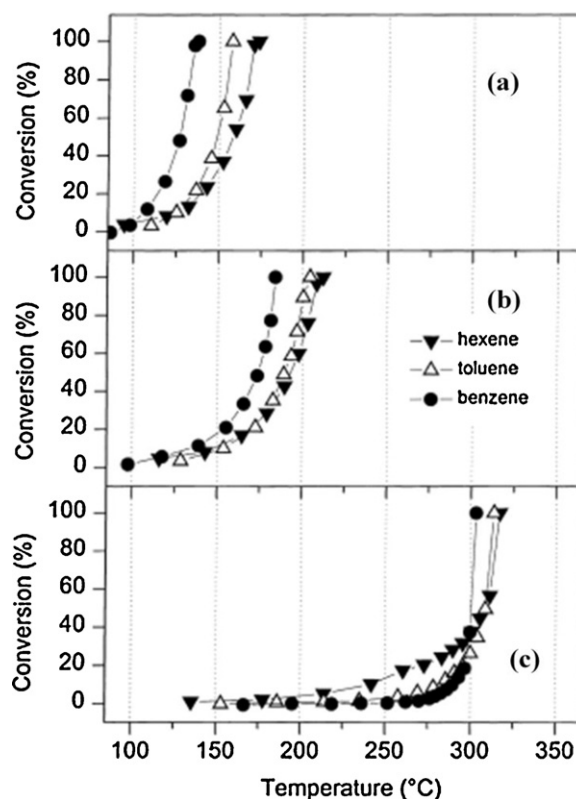

Fig. 1. Conversion versus temperature curves for the separate reactions of hexene, benzene and toluene over Pt/Al$_2$O$_3$ monolith. (a) In ~0.6% O$_2$/He; (b) in ~0.1% O$_2$/He; (c) in 1% CO/~0.6% O$_2$/He [25].

such as a low mass transfer inside capillary channels and sensitivity to clogging by coke agglomerates.

The catalytic activity depends on the noble metal and varies with the nature of VOC: alkane, alkene, aromatics. Pt and Pd over alumina were found both highly active for the oxidation of benzene and butanol, while ethyl acetate was more difficultly oxidized. Moreover, Pd performs better than Pt [11]. The oxidations of benzene, toluene and 1-hexene, alone and in mixtures with isooctane and carbon monoxide, have been investigated over alumina-supported platinum, palladium and rhodium cordierite monoliths, under different conditions [25]. Each metal exhibits a different activity order for the individual reactions. The difference is greatest with rhodium, which is the most active for hexene oxidation but poorly active for oxidation of the aromatics. Platinum is the most effective with benzene and palladium with toluene. Inclusion of CO in the reaction mixture greatly inhibits hydrocarbons oxidation on Pt, to a less extent on Pd. In Fig. 1 conversion curves versus temperature for the oxidation of hexene, toluene and benzene over Pt/Al$_2$O$_3$ at different oxygen concentration, with or without CO are displayed. With higher oxygen concentration and no CO (Fig. 1a) removal of each hydrocarbon is complete below 200 °C with benzene oxidized at the lowest temperature, followed by toluene and hexene. With lower oxygen concentration, the reactivity order is the same but the temperatures required for complete oxidation are raised by 40–50 °C (Fig. 1b). In the presence of CO the temperature required for each reaction is 100 °C higher (Fig. 1c). Moreover, CO inhibition is more drastic for benzene and toluene oxidation than for hexene. That is because hexene competes with CO better than benzene and toluene. The different activity trends observed for the investigated Pt, Pd and Rh alumina catalysts have been rationalized in terms of the relative strengths of adsorption–desorption of the reactants on the different metals [25]. It is worth noting that adsorption–desorption phenomena of VOCs over the catalyst
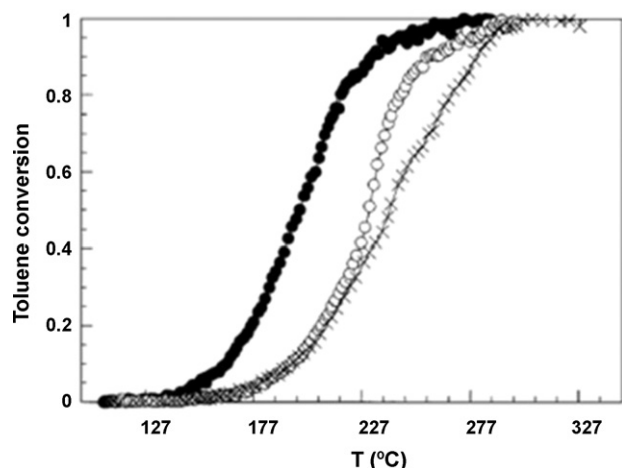
Fig. 2. Toluene oxidation curves over Pt/Al_2O_3 catalysts reduced at 300 °C and prepared from different platinum precursors: (●) Pt_{NH_3}/Al_2O_3, (○) Pt_{Cl_4}/Al_2O_3, and (×) Pt_{Cl_6}/Al_2O_3 [15].

surface are strongly enhanced by the exothermic character of the reaction and can influence the conversion curves in terms of CO_2 peaks higher than 100% conversion [26].

The effectiveness of Pt/γ-Al_2O_3 catalysts for the oxidation of not halogenated VOCs, such as *n*-hexane, methanol, *n*-butyl-amine, toluene, propane and propene, has been claimed by several authors [17,19,27,30,31]. Moreover, in comparison with Au-containing systems and Co_3O_4–CeO_2 mixed oxides, Pt catalysts are superior [13,31]. However, it is well-known phenomena that the oxidation activity of Pt is strongly suppressed by the presence of carbon monoxide [25,32]. Addition of Au/TiO_2 to Pt/Al_2O_3 enhances substantially the C_3H_6 oxidation over Pt thanks to the high activity of gold towards CO [30].

2.2. Influence of preparation method, support porosity, chlorine poisoning and metal particle size

It is well-known that the preparation method and the nature of metal precursors used, such as chlorinated or nitrate salts, can affect the catalyst properties. Catalysts containing platinum group metals are commonly prepared by impregnation of oxide supports with chlorine-containing salts, followed by calcination. Oxidative treatments in dry air are ineffective for removing residual chlorine. A pretreatment under wet stream is needed to completely eliminate chlorine as HCl [15]. On the other hand, the use of poisoned catalysts for oxidation reactions can involve Cl^- mobilization from the alumina support, to the Pt particles with consequent activity decrease. Further reaction would eliminate all the residual chlorine, due to the water formation [15,16,24]. Formation of stable and scarcely reducible MO_xCl_y species also occurs for Pd and Rh catalysts prepared by chlorinated precursors [33,34].

The inhibitory effects of chorine have been attributed to several causes. The use of chlorinated precursors can lead to high metal dispersion, causing complete oxidation of the noble metal under reaction conditions and, consequently, to a lower catalytic activity [15,35]. A partial blockage of metal active sites by chlorine has been also suggested, decreasing their ability to chemisorb reactant molecules [35–37]. Moreover, formation of less active oxychlorinated, MO_xCl_y, species occurs [15,16,24,33,34].

In Fig. 2 the toluene oxidation curves obtained after reduction at 300 °C of Pt/Al_2O_3 catalysts prepared from different precursors are shown [15]. Pt_{NH_3}/Al_2O_3 prepared by $Pt(NH_3)_4(OH)_2$, is the most active, both chlorinated catalysts are less active and have similar temperature of 50% of toluene conversion. But they differ in the
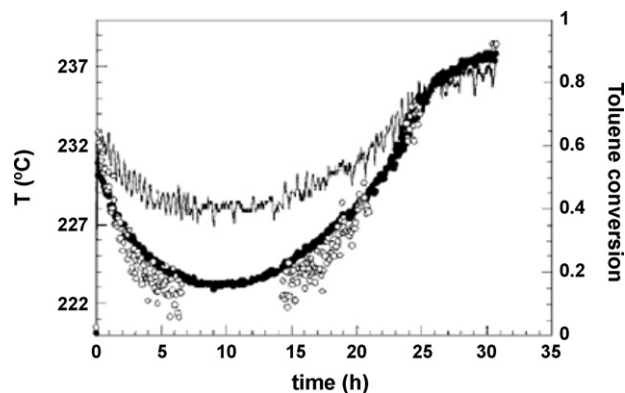

Fig. 3. Stability test of Pt_{Cl_4}/Al_2O_3 in toluene oxidation reaction at 214 °C for 30 h. (Line) Temperature at the bed inlet; (●) CO_2 signal; (○) toluene signal [15].

temperature at which 90% of conversion is reached, Pt_{Cl_6}/Al_2O_3 being worse. So it seems that the more chlorinated is the Pt precursor, lower is the toluene oxidation activity. In order to explain the reasons of the different performances, the stability of a catalyst prepared from chlorinated precursor, Pt_{Cl_4}/Al_2O_3, was tested by running the catalyst, pre-reduced in H_2 at 300 °C for 1 h, under toluene/oxygen reaction mixture at 214 °C for 30 h (Fig. 3). The initial toluene conversion starts to decrease almost immediately with a minimum (<20%) reached after 10 h of reaction, producing also a bed inlet temperature decrease of 5 °C. From that time on, there is a conversion increase reaching 90% after 30 h of reaction, while the initial conversion was 55%. So the catalyst seems become more active after the stability test.

In Fig. 4 toluene conversion curves on the catalyst Pt_{Cl_4}/Al_2O_3 subjected to different pre-treatments and after 30 h of stability test (see Fig. 3) are compared. As can be seen, pre-treatments under wet air at 500 °C and under wet He at the same temperature produce the most active Pt_{Cl_4}/Al_2O_3 catalyst, which performs similarly as after the stability test. Therefore, it can be concluded that the activation under wet stream and/or under reaction conditions, for long time, corresponds mainly to the elimination of chlorine residuals, poisoning the metal active sites. On the other hand, the catalyst reduction at 300 °C produces both, transition of the chlorine from the surface of Pt to its interior and from the surface of Pt to the alumina surface [15,16]. The start of toluene oxidation generates segregation of the chlorine from the bulk to the Pt surface as well

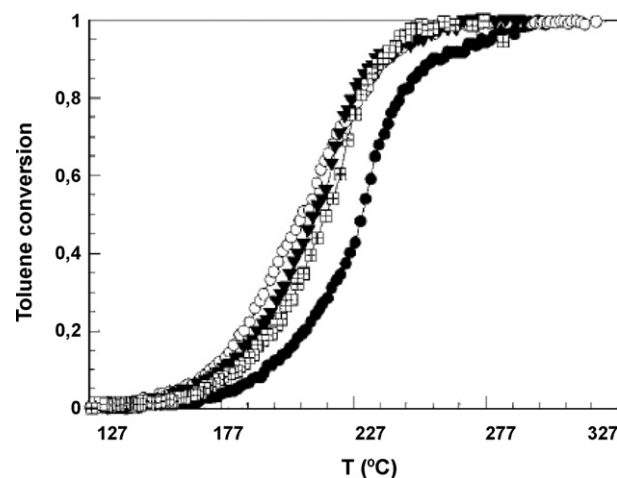**Fig. 4.** Toluene oxidation curves over Pt_{Cl_4}/Al_2O_3 after different pre-treatments: (●) reduction in H_2 at 300 °C for 1 h; (○) oxidation under wet air at 500 °C for 18 h; (▼) after 18 h under wet He at 300 °C; (▣) after 30 h of stability test at 214 °C [15].

Table 1
Main physico-chemical characteristics of Pt/Al$_2$O$_3$ catalysts [19].

Catalysts	Supports	Platinum precursor salt	Specific surface area (m^2/g)	Pt (wt%)	Pt dispersion(%)	d_{Pt} (nm)[a]
P1	Rhodia (SPH 569) calcined at 500 °C	Pt(NH$_3$)$_4$(OH)$_2$	146	1.5	35	3.2
P2	Rhodia (SPH 569) calcined at 500 °C	H$_2$PtCl$_6$	147	1.1	60	1.9
P3	Rhodia (SPH 569) calcined at 500 °C	Pt(NH$_3$)$_4$(OH)$_2$	133	0.8	62	1.8
P4	Alfa Aesar	Pt(NH$_3$)$_4$(OH)$_2$	76	0.9	56	2.0
P5	Alfa Aesar calcined at 500 °C	Pt(NH$_3$)$_4$(OH)$_2$	74	0.9	66	1.7
P6	Pall Exekia	Pt(NH$_3$)$_4$(OH)$_2$	223	0.8	55	2.0
P7	Alfa Aesar calcined at 500 °C	H$_2$PtCl$_6$ + HNO$_3$	77	1.0	48	2.3
P8	Alfa Aesar	Pt(NH$_3$)$_4$(OH)$_2$	80	0.56	83	1.4

[a] d_{Pt} is the Pt metal particle diameter.

as back spillover of the chlorine from the support to the metal. Both these effects may explain the lower activity (Fig. 4).

The detrimental effect of chloride on the complete oxidation of propene and toluene over Pt/γ-Al$_2$O$_3$ catalysts was also confirmed in a recent study, where Pt catalysts with different loadings (0.5, 1, and 1.5 wt%) were prepared by impregnation method from a solution of Pt(NH$_3$)$_4$(OH)$_2$ or H$_2$PtCl$_6$ on three commercial supports, γ-Al$_2$O$_3$ (Rhodia-SPH569), γ-Al$_2$O$_3$ (Pall Exekia) and γ-Al$_2$O$_3$ (Alfa Aesar) [19]. The influence of supports with different surface areas and the effect of Pt catalysts dispersion were also addressed.

The BET surface area of these supports covers a broad range from 80 m^2/g for Alfa Aesar alumina to 150 m^2/g for Rhodia and to 225 m^2/g for the Pall Exekia one. In Table 1 the main physico-chemical characteristics of the prepared catalysts are listed. Due to high cost, the noble metal content must be as low as possible and the highest accessible metallic fraction should be obtained. Generally, highly dispersed noble metal catalysts were obtained using γ-alumina as support, as here reported. By comparing propene conversion as a function of the temperature for samples P3, P5, P6 and P7, containing almost the same Pt loading (∼1 wt%), with dispersion within the range 50–60%, but prepared on different alumina supports, it results that the activity trend is similar irrespective of the nature of the supports. In all cases, conversion of propene begins at 100 °C, 50% of propene conversion occurs at around 150 °C and, finally, full conversion is achieved at 170 °C. These results suggest that propene oxidation takes place on platinum sites and the support does not play any significant role in the catalytic mechanism.

In Fig. 5 the catalytic conversion of propene and toluene are shown for the catalysts P1, P5 and P8, containing 1.5, 0.9 and 0.56 wt% of Pt, respectively. Complete oxidation of propene occurs at 140 °C for P1, at 152 °C for P5 and only at 175 °C for P8. Therefore,

the propene conversion curves are shifted towards lower temperatures by increasing the Pt loading.

Looking at the conversion curves, it appears that propene oxidation is strongly temperature dependent and abruptly increases with temperature. For instance, propene conversion on P5 drastically increased from 40% to 80% for a slightly temperature change of <5 °C. This is in good agreement with other results [38] reporting fast process of light off for complete oxidation of propene on Pt based catalysts.

In the case of toluene oxidation, the catalytic activity also increased with the Pt loading. The catalyst with the highest Pt content, P5, gave full conversion at 227 °C, while the temperature slightly increased to 250 °C when the Pt content decreased to 0.56 wt% (P8). Similar trends have been previously reported in the literature [27], where the catalytic combustion of toluene (600 ppm) was studied over Pt/γ-Al$_2$O$_3$ spheres. The authors observed an increase of the temperature of 50% of toluene conversion from 180 °C to 263 °C when Pt loading decreased from 0.4 to 0.05 wt%.

In order to better compare the above Pt catalysts having different metal content and dispersion, the catalyst intrinsic rates for VOC conversion expressed as mol VOC s^{-1} g$_{Pt}^{-1}$ are illustrated in Fig. 6 with respect to the temperature and the Pt loadings. Due to the different Pt dispersion (Table 1) the plots of catalytic intrinsic rate as a function of the temperature are not superimposed. Best catalyst performance for propene combustion was achieved for the catalyst P1 which has the lowest dispersion (35%). Intrinsic catalytic activity of P1 was higher than that of P8 which has the highest Pt dispersion (83%). The same trend was observed for toluene oxidation: larger Pt particles exhibited better activity.
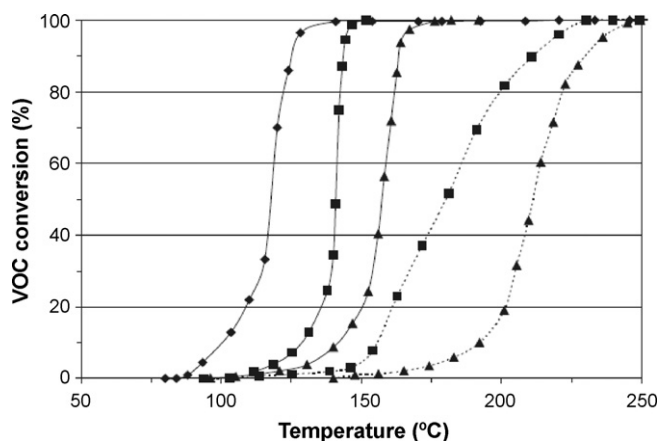

Fig. 5. VOC conversion versus temperature for three Pt/Al$_2$O$_3$ catalysts, containing different Pt loadings ((▲) P8 0.5 wt%, (■) P5 1.0 wt%, and (◇) P1 1.5 wt%). Full line: propene combustion and dotted line: toluene combustion. Reactant mixture composition: 1000 ppm VOC + 9% O$_2$, rest He. Catalyst weight 200 mg, total gas flow rate: 120 mL min^{-1} [19].

Fig. 6. Variations of the intrinsic activity versus temperature for three Pt/Al$_2$O$_3$ catalysts with different Pt loadings ((▲) P8 0.5 wt%, (■) P5 1.0 wt%, and (◇) P1 1.5 wt%). Full line: propene combustion; dotted line: toluene combustion. Reactant mixture composition: 1000 ppm VOC + 9% O$_2$, rest He. Catalyst weight 200 mg, total gas flow rate: 120 mL min^{-1} [19].
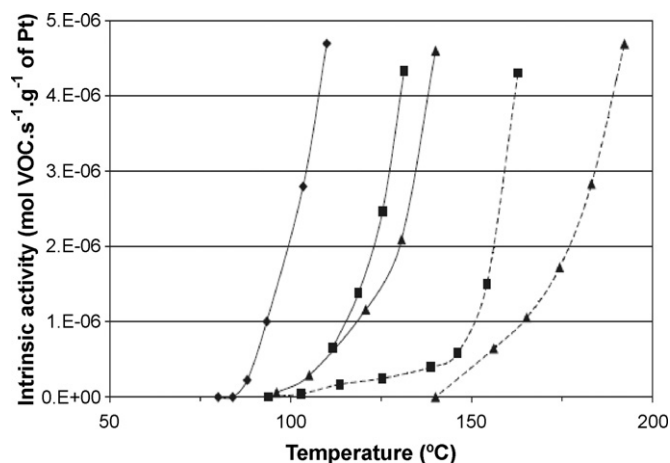
Table 2
Comparison between propene and toluene oxidation on the catalyst P8 (0.56 wt% Pt). Reactants mixture: VOC 1000 ppm, O_2 9%, rest He. Catalyst weight: 200 mg and total flow rate: 120 mL min^{-1} [19].

VOC nature	Start-up temperature (°C)	T_{50} (°C)[a]	T_{100} (°C)[b]	TOF[c] ($\times 10^4$ s^{-1}) at 150 °C
Propene	110	157	170	23.5
Toluene	140	211	250	0.94

[a] T_{50}: temperature of 50% conversion.
[b] T_{100}: temperature of 100% conversion.
[c] TOF (s^{-1}): turnover frequencies calculated as TOF = r(100MPt/dispersion) [19].

The effect of metal particle size on VOCs catalytic oxidation has been the focus of extensive studies for several decades. As the dimension of a metal particle approaches the nanometer range, its properties can be expected to deviate from those of the bulk due to the variations in electronic structure and to changes in the nature of surface adsorption sites. Accordingly, particle size sensitivity for propylene oxidation over Pt and Pd alumina-supported catalysts has been already reported in the literature [14,24,39–41] and there is a general agreement that the oxidation rates increase with increasing metal particle sizes. This finding concerns also toluene oxidation. Very few papers deal with the structure sensitivity of aromatic hydrocarbons combustion on Pt based catalysts. The toluene oxidation rate over Pt/Al$_2$O$_3$ catalysts was found about 10 times higher for Pt crystallites size of 15.5 nm compared to one of 1.0 nm [17]. Moreover, a decrease of the Pt–O bond strength with the enlargement of the Pt crystallite size was observed, leading to more reactive adsorbed oxygen species on Pt sites [17,41,42]. The oxidation of benzene over Pt catalysts on different supports was studied [43]. The dependence of TOF on Pt particle size was strong in the case of Pt/γ-Al$_2$O$_3$ catalysts.

In Table 2 propene and toluene reactivity on the catalyst P8, containing 0.56 wt% of Pt, are compared in terms of temperatures of start-up, of 50 (T_{50}) and 100% conversion (T_{100}), TOF (turnover frequencies) values. It results that propene oxidation occurs at lower temperatures than toluene (Fig. 5). Moreover, in the case of toluene the shape of light-off curves is extended on a larger range of temperature, according to a lower toluene oxidation activity.

Based on the so far reported data, it emerges that Pt dispersion is a major factor affecting the intrinsic activity of VOCs oxidation. The effects of other parameters, such as the nature of the support and the acid-base properties, on the oxidation activity of supported noble metals were also addressed in the literature. Detailed investigations of the influence of different types of alumina and silica oxides and their porosity on the C$_3$H$_6$ oxidation in presence of NO have been reported for a series of Pt catalysts [40]. To this purpose, Pt was deposited by wet impregnation of different supports, meso-, microporous and non-porous alumina and silica oxides, with

chlorine-free or chlorinated platinum precursors. For a given preparation procedure, the Pt dispersion was dependent on the support porosity. Very high dispersion (93–100%) was achieved on microporous silica, while over non-porous silica and alumina catalysts with moderate dispersion (~50–60%) were formed. A large range of Pt dispersion was obtained over mesoporous supports, with value ranging between 55% and 94% for Pt/alumina and between 23% and 97% for Pt/silica catalysts.

According to the literature, it was confirmed that Pt dispersion was a major factor affecting the intrinsic oxidation activity of Pt catalysts. In general, larger particles led to higher intrinsic activity for both, alumina and silica oxides. The other factors, as nature (alumina and silica), acid-base properties and porosity of the support, are of minor importance. Moreover as novelty, the paper [40] highlighted the changes in particle size distribution occurring under the reaction mixture, showing the initial dispersion of the catalysts is not representative of the state after activation under reaction mixture. As it concerns the catalysts ageing, it was found that the dispersion decreased more strongly with alumina than with silica and, in the case of alumina, with a chlorine-containing precursor. However, the relationship between the initial and final dispersion was not completely clear.

2.3. Mixture effects and influence of water on the catalytic activity

Industrial oxidation processes commonly contain a mixture of VOCs rather than a pure component. Therefore, it is important to know whether the catalytic performances of a catalyst in the oxidation of a given component are influenced by the presence of other components which could competitively adsorb over the catalyst surface.

Moreover, water vapor is usually present in industrial flue gases, thus the effect of water vapor on the catalytic activity needs investigation. In general, water vapor has been found to act as an inhibitor of VOC oxidation. Addition of water was reported to inhibit the oxidation of propane and propene hydrocarbons on Pt and Pd
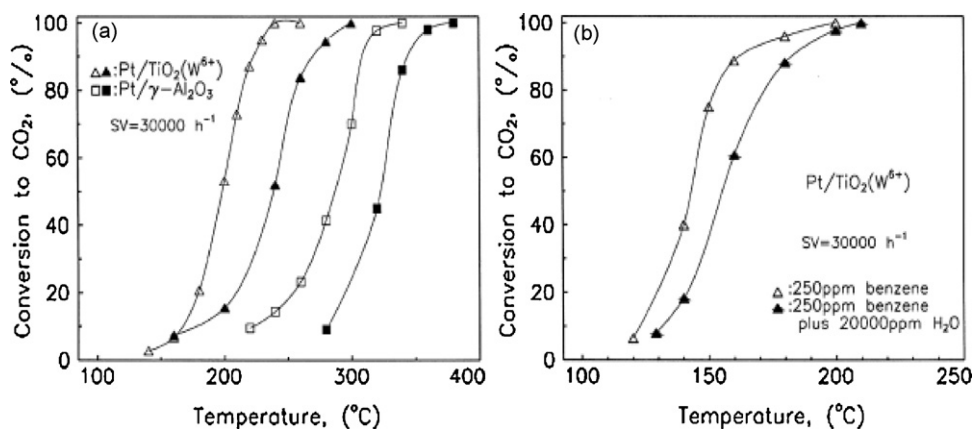

Fig. 7. Effect of water vapor on the conversion of (a) ethylacetate and (b) benzene to CO$_2$ as a function of temperature over Pt catalysts (open symbols: 250 ppm VOC; filled symbols: 250 ppm VOC + 20 000 ppm H$_2$O) [44].
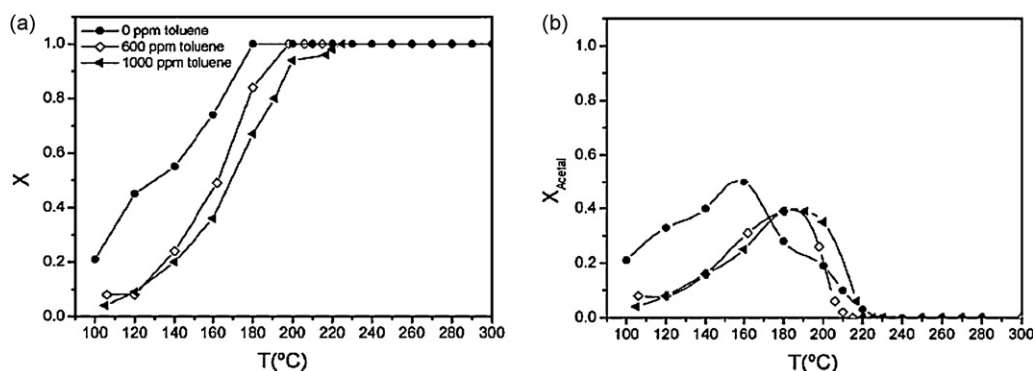
Fig. 8. (a) Ethanol conversion curves alone and in binary mixtures with toluene, In the presence of a Pt(1.1%)/TiO$_2$ catalyst. (b) Conversion into acetaldehyde [47].

supported catalysts [24]. The poisoning effect was explained by a decrease of active surface sites.

The effect of water vapor on the deep oxidation of ethylacetate and benzene over Pt/γ-Al$_2$O$_3$ and Pt/TiO$_2$ (W^{6+}) catalysts [43,44]. Moreover, the effect of a benzene–ethylacetate–water mixture was examined employing a feed mixture containing 250 ppm of each VOC in air and 2% of water vapor.

The presence of water vapor in the gas stream inhibits the deep oxidation of ethylacetate and benzene was investigated over Pt/γ-Al$_2$O$_3$ and Pt/TiO$_2$–WO$_3$ catalysts and the required increase in reaction temperature in order to achieve the same conversion level is in the order of 10–40 °C [43]. The conversion curves to CO$_2$ without water and in presence of 2% of water vapor (20,000 ppm) are shown in Fig. 7a and b. It is important to observe that while water suppresses deep oxidation of ethylacetate to CO$_2$, nevertheless it promotes the decomposition of ethylacetate [44]. This probably occurs because the strong adsorption of water on the metal sites suppresses the conversion to CO$_2$ of ethylacetate that in the presence of water hydrolyzes to ethanol and acetic acid. In the case of binary benzene–ethylacetate mixtures, benzene oxidation is strongly inhibited by ethylacetate, while ethylacetate oxidation is not influenced by the presence of benzene [43]. This phenomenon implies a different interaction mechanism of benzene and ethylacetate with the catalyst. Previous studies from the same group [45] have shown that benzene does not interact as strongly as ethylacetate does with the support surface. Therefore, the benzene coverage of the (W^{6+})-doped TiO$_2$ support is expected to be very low under oxidation of benzene–ethylacetate mixtures.

In order to avoid the inhibition effect of water, the use of Pt over hydrophobic supports, such as porous styrene divinylbenzene copolymer (SDB), should be mentioned. Such systems have been investigated for toluene oxidation [46]. Preliminary results were promising because the oxidation reaction was enhanced by expelling water from the catalyst surface. However, sintering of Pt clusters seemed to be severe on SDB that would require further investigations.

Inhibiting effects during oxidation of benzene–butanol mixtures over Pt and Pd catalysts have been also reported [11]. For both catalysts, benzene oxidation was almost completely suppressed by the presence of butanol in the reaction mixture. In the case of Pt catalysts, butanol oxidation is also inhibited by benzene. On the contrary, a positive effect of benzene on butanol conversion was observed over Pd catalysts [11].

Experiments with ethanol/toluene mixtures performed with a Pt (1.1 wt%)/TiO$_2$ catalyst [47] have confirmed a mutual inhibitory effect. Toluene inhibits the partial combustion of ethanol (especially at low-temperature) by decreasing the acetaldehyde yield.

In Fig. 8a the conversion curves of ethanol alone and in binary mixtures with toluene are plotted. In Fig. 8b the conversion into acetaldehyde is shown. The curves corresponding to the conversion of ethanol and its conversion to acetaldehyde are shifted to higher temperatures as toluene concentration increases. Moreover, the amount of acetaldehyde formed is smaller when toluene is added to ethanol. Ethanol also has an inhibition effect on the total oxidation of toluene, although the effect is not as pronounced as with the addition of toluene to ethanol.

2.4. Reaction mechanisms

The influence of reactants concentration on the catalytic rate of supported noble metal catalysts has been extensively studied and different reaction orders in VOC and O$_2$ were found depending on the nature of the catalyst [11,14,17,19,48–50]. The reaction order with respect to benzene, butanol and ethyl acetate over Pt and Pd/alumina-supported catalysts was positive in all cases, with values in the 0–1 range, while the reaction order with respect to oxygen was observed to be close to zero or negative [11]. For propene, 1-hexene and toluene oxidation over supported Pt, Pd, Rh catalysts positive orders in O$_2$ and negative order in olefins were reported [14,19,48,49]. Depending on the partial reaction order, different reaction mechanisms have been proposed for VOCs oxidation: the Langmuir–Hinshelwood (L–H) mechanism in which the controlling step is the surface reaction between two adsorbed molecules on analogous active sites; the Eley–Rideal (E–R) mechanism in which the controlling step is the reaction between an adsorbed molecule and a molecule from the gas phase; the Mars–van Krevelen (MVK) which is an oxidative–reductive mechanism involving reaction of VOC molecule and oxygen on different redox sites. This mechanism has been widely used for the oxidation of organic compounds [51,52].

The favoured mechanism in the literature for Pt, Pd, Rh catalysts is the L–H, involving reaction between adsorbed molecules on metal sites [48,49]. The reaction order in VOC depends on the nucleophilic character of the organic molecule. A negative order in the unsaturated hydrocarbon is generally found, due to its strong adsorption on the Pt, Pd surface through π-bonds and backdonation from the metal to the π*-hydrocarbon orbitals.

On the other hand, it was demonstrated that complete oxidation of toluene and methyl ethyl ketone over Pt supported on Al$_2$O$_3$/Al monoliths is not affected by the presence of 2-propanol, suggesting that they are oxidized directly from the gas phase with the oxygen atoms chemisorbed on Pt (E–R mechanism) [53]. A similar mechanism was, recently, invoked for the oxidation of toluene over a Pt(1.1 wt%)/TiO$_2$ catalyst [47].
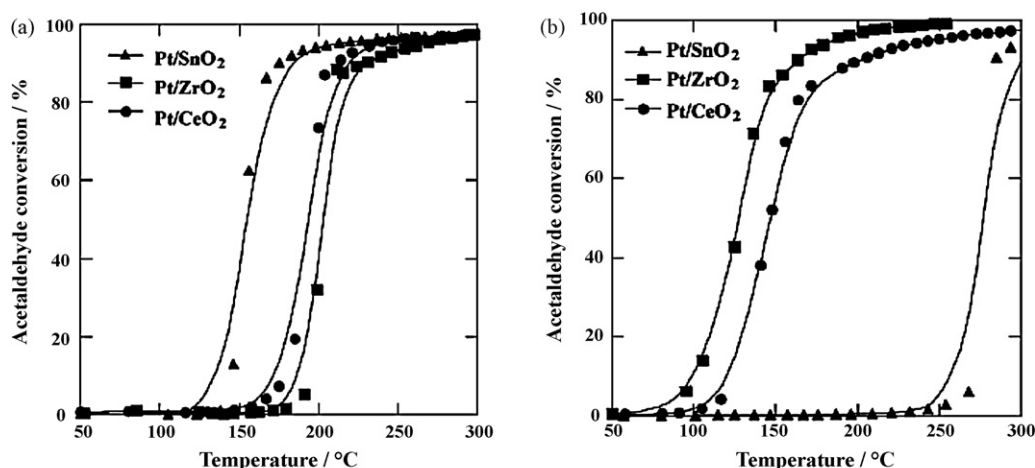
Fig. 9. Acetaldehyde conversion over oxide-supported 1.0 wt% Pt catalysts: (a) as-calcined catalysts; (b) catalysts reduced at 400 °C. Reaction conditions: acetaldehyde 1.0%, air 99.0%; space velocity: 10,000 L kg^{-1} h^{-1}; heating rate: 100 °C h^{-1} [57].

The occurrence of MVK mechanism has been also widely reported for hydrocarbons oxidation over Pt catalysts [17,50,54,55]. For toluene oxidation performed over 0.12 wt% Pt/Al$_2$O$_3$ catalysts with two different crystallite sizes, 1.0 and 15.5 nm, the reaction order with respect to both reactions was found dependent on the mean crystallite size of Pt [17]. For the sample with a mean crystallite size of 1.0 nm with increase of temperature from 132 °C to 164 °C the reaction order with respect to toluene increases from 0.1 to 0.9, while the reaction order with respect to oxygen decreases to almost zero. On the contrary, for a sample with mean Pt size of 15.5 nm the reaction rate was of zero order with respect to toluene and close to the first order with respect to oxygen, in the whole range of concentrations and temperatures investigated.

The validity of MVK mechanism was confirmed by fitting the catalytic oxidation data of benzene, toluene and *n*-hexane, both alone and in binary mixtures, over a commercial Pt on γ-alumina catalysts [50]. The oxidation reactions of cyclopentane and methane on Pt/Al$_2$O$_3$ catalysts, with different Pt and residual chlorine loading, were interpreted by applying a MVK mechanism [54]. However, it emerged that the two reactions proceed via different rate-determining steps. Cyclopentane was oxidized on metallic Pt sites via a surface redox mechanism, being the dissociative adsorption of oxygen on Pt the rate-determining step. While, for methane oxidation a MVK reduction–oxidation pathway, involving as rate-determining step the abstraction of the first hydrogen of the adsorbed CH$_4$ molecule, was invoked.

2.5. Recent results on Pt, Pd, Rh supported over transition metal oxides: role of the support and redox properties

On the basis of the so far reported data, Pt on high-surface area γ-Al$_2$O$_3$, as powder or wash-coated on a monolith is the most commonly used catalyst for VOCs abatement. At the same time, a wide variety of supported Pt, Pd metals on reducible oxides are currently explored [56–61]. Pd/Pt catalysts, prepared on metallic CrAl steel and promoted by small amount of Co$_3$O$_4$ spinel highly dispersed on alumina layer, are active in combustion of diluted *n*-hexane [56]. According to the literature [12,13], small cobalt oxide spinel-type crystallites form active oxygen species and enhance the oxidation activity of supported PdO.

The VOCs oxidation activity is often related to the reduction properties of supported noble metals and is enhanced by the presence of platinum/palladium species easily reducible at low-temperature. On the other hand, reduction treatments greatly affect catalytic activity since active species and support oxides can interact strongly each other, depending on the nature of the support. Pt and Pd catalysts supported on SnO$_2$, ZrO$_2$ and CeO$_2$ oxides have been investigated in the catalytic combustion of acetaldehyde [57]. The effect of a reduction treatment, at 400 °C for 15 min in 50% H$_2$/N$_2$, on the catalytic activity was evaluated in comparison with the as-calcined catalysts (treatment at 400 °C for 30 min in air). Among the as calcined samples, SnO$_2$-supported Pt and Pd showed the highest activity at low temperatures, while the activity was significantly degraded by reduction treatment in H$_2$ atmosphere, due to the formation of an inter-metallic compound. On the contrary, the activity of ZrO$_2$- and CeO$_2$-supported catalysts was improved by reduction treatment. In Fig. 9a and b the acetaldehyde conversion curves over oxide-supported 1.0 wt% Pt catalysts as-calcined (a) and after reduction at 400 °C (b) are compared. The catalytic activity of as-calcined SnO$_2$-supported catalysts was related to the presence of Pt/Pd oxide species easily reducible at room temperature. Such species disappeared after reduction treatment at 400 °C due to the formation of not active inter-metallic phases, PtSn and Pd$_3$Sn$_2$. In the case of ZrO$_2$- and CeO$_2$-supported catalysts, Pt and Pd particles were reduced in metallic state after hydrogen treatment, resulting in the improvement of the activity with respect to the as-calcined samples.

Novel Pd catalyst supported on Ce-, La-, Pr- and Zr-pillared montmorillonite have been prepared and tested for the catalytic combustion of toluene, acetone, and ethyl acetate [58]. In all cases, full conversion was achieved between 220 °C and 260 °C. PdO/La/Zr-montmorillonite was the most active catalyst or performed similarly to PdO/Ce/Zr-montmorillonite in the case of acetone oxidation. The addition of promoters, such as CeO$_2$, La^{3+}/Bi^{3+} doped CeO$_2$–ZrO$_2$ oxides, has been successfully applied to increase the activity and thermal stability of Pt, Pd alumina-supported catalysts for toluene oxidation as well as for the abatement of VOC emissions from wood combustion in domestic fireplaces and stoves [59–61]. Doping CeO$_2$–ZrO$_2$ solid solution with La^{3+} ions increased the lattice oxygen mobility of ceria and enhanced the dispersion of Pd, thus making the catalyst with excellent toluene oxidation activity and high-temperature stability [59]. The participation of lattice oxygen species of the support was also claimed for a Pt (7 wt%)/(16 wt%)Ce$_{0.64}$Zr$_{0.15}$Bi$_{0.21}$O$_{1.895}$/γ-Al$_2$O$_3$ catalyst giving complete oxidation of toluene at low-temperature (120 °C) [60].

Pollutant characterization of domestic fireplaces, in different working conditions (ignition, normal, low-charge) showed that methane is the dominant compound of the released gases, while CO and other VOCs do not represent more than 6% of the initial car-

Table 3
Efficiency of a Pt, Pd, Ce cordierite catalyst coupled with an electric heating system for CO and VOCs oxidation emitted from a fireplace of old generation [61].

Working conditions	Without catalyst	With cordierite catalyst	With cordierite catalyst and heating system
CO (%)			
Ignition	0.22[a]	0.18[a]	0.11[a]
Normal	0.3 ± 0.1	0.2 ± 0.1	0.2 ± 0.04
Low-charge	1.12[a]	1.83[a]	0.31[a]
VOC (ppm)			
Ignition	430[a]	586[a]	357[a]
Normal	640 ± 160	600 ± 170	960 ± 260
Low-charge	4203[a]	2882[a]	717[a]

[a] Only one concentration measured during a daily experiment.

Table 4
Efficiency of a Pt, Pd, Ce metallic catalyst coupled with an electric heating system for CO and VOCs oxidation emitted from a fireplace of old generation [61].

Working conditions	Without catalyst	With metallic catalyst	With metallic catalyst and heating system
CO (%)			
Ignition	0.22[a]	0.11[a]	0.05[a]
Normal	0.3 ± 0.1	0.09 ± 0.02	0.1 ± 0.01
Low-charge	1.12[a]	0.11[a]	0.17[a]
VOC (ppm)			
Ignition	430[a]	475[a]	288[a]
Normal	640 ± 160	560 ± 170	500 ± 100
Low-charge	4203[a]	1474[a]	1467[a]

[a] Only one concentration measured during a daily experiment.

bon content in wood [61]. The catalytic reduction of CO and VOCs in the fume was investigated using two catalytic systems. The active phase was composed by Pt, Pd and Ce supported on a cordierite monolith or on a metallic structure. In order to improve the activity of the catalyst when the temperature of fume is lower than 300 °C, an electric heating device was introduced. Such a system was more efficient than the cordierite catalyst achieving abatement of CO and VOCs with values close to 94% and 80%, respectively [61]. In Tables 3 and 4, the efficiency of the two catalytic systems was compared for CO and VOCs oxidation with an old generation fireplace.

Formaldehyde (HCHO) is one of the most toxic VOC compounds dominating in the indoor environment, therefore, its abatement is of significant practical interest at low temperature, especially at room temperature. Several noble metal catalysts have been investigated, however oxidative decomposition of formaldehyde occurred only above ~100–150 °C [62–64]. Recently, catalytic oxidation of formaldehyde was achieved over Pt/TiO_2 catalysts at room temperature or below 100 °C [65–67]. TiO_2 supported noble metal

(Au, Rh, Pd and Pt) catalysts were tested for the catalytic oxidation of formaldehyde. It was found that the order of activity was $Pt/TiO_2 \gg Rh/TiO_2 > Pd/TiO_2 > Au/TiO_2 \gg TiO_2$. HCHO could be completely oxidized into CO_2 and H_2O over Pt/TiO_2 even at room temperature. In contrast, the other catalysts were much less effective for HCHO oxidation at the same reaction conditions. HCHO conversion to CO_2 was only 20% over the Rh/TiO_2 at 20 °C. The Pd/TiO_2 and Au/TiO_2 showed no activities for HCHO oxidation at 20 °C [66]. In Fig. 10, HCHO conversions over the above mentioned catalysts are shown.

When comparing the HCHO oxidation activity of a series of noble metals (Pt, Pd, Rh) over TiO_2, Pt was found the most active [67]. Using other supports, such as $Ce_{0.8}Zr_{0.2}O_2$, $Ce_{0.2}Zr_{0.8}O_2$, SiO_2 instead of TiO_2, the superiority of Pt/TiO_2 was again confirmed. Moreover, Pt loading on TiO_2 has a great effect on the catalytic activity. In Fig. 11 the effects of Pt loadings, varied from 0.01 to 1 wt%, on TiO_2 are displayed. The 0.6 wt% characterized by well dispersed Pt particles was the most active giving at room temperature 40% of HCHO conversion and full oxidation at 90 °C, however, increasing
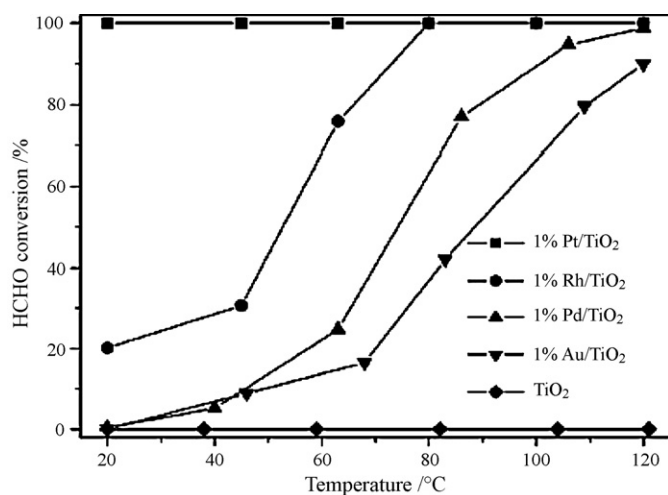

Fig. 10. HCHO conversions over TiO_2 (◇); Pt/TiO_2 (■); Rh/TiO_2 (●); Pd/TiO_2 (▲); Au/TiO_2 (▼) catalysts at various temperatures. Reaction conditions: HCHO 100 ppm, O_2 20 vol.%, He balance, total flow rate: 50 cm³ min⁻¹, and GHSVs: 50,000 h⁻¹ [66].
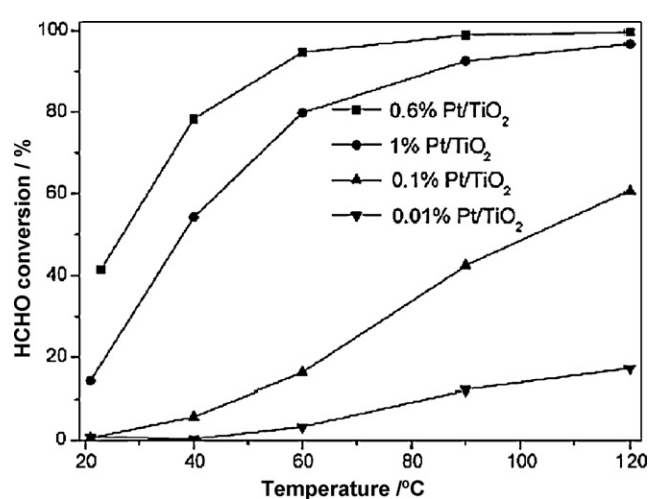

Fig. 11. Temperature dependence of HCHO conversions for Pt/TiO_2 catalysts with different Pt loadings. Reaction conditions: HCHO 100 mg/m³, O_2 22 vol.%, N_2 balance, total flow rate 1200 cm³/min and GHSV = 300,000 cm³/g h [67].

HCHO concentration and space velocity an inhibiting effect on the catalytic activity was observed.

Recently, it was reported that the preparation method can have a significant effect on the performance of Pt, Pd and Rh/TiO$_2$ catalysts towards total oxidation of CO, ethanol and toluene [47]. The catalysts were prepared by liquid phase reduction deposition (LPRD) and by incipient wetness impregnation (IMP). The preparation method had a significant effect on the dispersion of the metallic phase and subsequently on the oxidation activity. In VOC oxidation, Pt/TiO$_2$ was the best catalyst, the following performance trend being observed: Pt/TiO$_2$ > Pd/TiO$_2$ ≫ Rh/TiO$_2$ for both preparation methods. Ethanol and toluene oxidation over Pt and Pd catalysts were found to be structure sensitive reactions.

3. Discussion

An important aspect concerning the oxidation of VOC over noble metal catalysts is that the reaction is generally recognized to be structure sensitive. The effect of the Pt particle size on the catalytic combustion of different hydrocarbons has been extensively studied. Turnover rates strongly increase with increasing Pt particle size. This size dependency may be linked to several factors, such as redox properties, strength of the Pt–O bond, reaction mechanism. Cyclopentane oxidation turnover frequencies (TOF) increased dramatically with increasing Pt crystallite size of Pt/Al$_2$O$_3$ catalysts, while TOF values for methane oxidation increased only three times for catalysts with 65 and 15% metal dispersion [54]. These results were interpreted on the basis of two MVK reaction mechanisms involving different rate-determining steps.

Besides the MVK mechanism, the L–H mechanism (reaction with chemisorbed reactant) and the E–R mechanism (reaction with gaseous reactant) are also widely invoked for the oxidation of VOCs over noble metals.

The validity of each mechanism strongly depends on the catalyst (noble metal and nature of the support) as well as on the character of the VOC molecule and it is difficult to generalize. The validity of L–H mechanism for oxidation of olefins and aromatics over Pt/γ-Al$_2$O$_3$ catalysts is supported by the nature of the noble metal capable of getting electron transfer from the aromatic ring to the unoccupied d-orbitals and backdonation from the metal to the π*-hydrocarbon orbitals. Accordingly, the occurrence of such a mechanism has been proved for oxidation of benzene, toluene, propene and 1-hexene as well [11,19,48,49]. On the other hand, it was also reported for Pt supported on Al$_2$O$_3$/Al monoliths and for a Pt (1.1 wt%)/TiO$_2$ that toluene oxidation takes place via (E–R) mechanism in which toluene reacts mainly in the gas phase with oxygen chemisorbed on the Pt metal surface [47,53].

Water vapor is present in industrial flue gases, which usually consist of mixture of VOCs rather than a pure component. Therefore, it is fundamental to investigate the effect of water vapor and of a VOC mixture on the activity of a given catalyst. Water vapor has been found to act as an inhibitor of VOC oxidation. Moreover, the catalytic performances in the oxidation of a given VOC molecule are influenced by the presence of a mixture, due to competitive adsorption phenomena and usually an inhibitor effect was reported. However, due to the complexity of the processes that take place during oxidation of mixture, it is difficult to predict the behavior of a catalyst and experimental verifications are required.

Pt on high-surface area γ-Al$_2$O$_3$, as powder or wash-coated on a monolith is the most commonly used catalyst for VOCs abatement. At the same time, a wide variety of supported Pt, Pd metals on reducible oxides are currently explored due to the peculiar properties of the supports. The VOCs oxidation activity is related to the catalysts reduction properties and is enhanced by the presence of

platinum/palladium species easily reducible at low-temperature. Moreover, it has been demonstrated that low-temperature catalytic oxidation of VOCs involves lattice oxygen species and the presence of noble metals can increase the oxide reducibility [59,60].

4. Conclusions

From the present review the following main results can be summarized: the catalytic incineration has become the most popular method for VOCs abatement being more versatile and economical than un-catalyzed thermal oxidation especially for low concentration of organic emissions (<5000 ppm). Based metal oxides and precious metals are used both for hydrocarbons and chlorinated hydrocarbons. Precious metals, especially Pt and Pd, dispersed over high-surface area γ-Al$_2$O$_3$ powder or wash-coated on a monolith, are preferred because of their better activity, resistance to deactivation and ability to be regenerated. The honeycomb structure of monolith substrates is necessarily used for industrial abatement of VOCs offering the major advantage of low-pressure drop due to its high open frontal area.

Generally, Pt is preferred to Pd although palladium seems more effective for ethyl acetate and toluene oxidation.

The catalytic performances of Pt supported samples are strongly affected by the presence of chlorine and the activity increases when successive cycles are performed due to the chlorine removal. Another important aspect concerning the oxidation of VOC over noble metal catalysts is that the reaction is generally recognized to be structure sensitive. The effect of the Pt particle size on the catalytic oxidation of different hydrocarbons has been extensively studied. Generally, the metallic particles size strongly affects the activity, larger Pt particles being more active. Other factors, such as the nature of the support (alumina or silica), the porosity and acid-base properties of the support influence to a less extent the catalytic performances of Pt catalysts.

Addition of water was proved to inhibit the oxidation of propane and propene hydrocarbons on Pt and Pd catalysts supported over oxides. Due to their hydrophilic surface the catalyst might be cloaked and the activity was reduced. The use of hydrophobic supports, such as porous styrene divinylbenzene copolymer (SDB) could represent an alternative, although further investigation is required in order to increase the stability of Pt particles.

Moreover, the catalytic performances in the oxidation of a given VOC molecule are influenced by the presence of a mixture of VOC compounds and usually an inhibitor effect was found.

Concerning the mechanism of VOCs oxidation, different orders of reaction in VOC and O$_2$ have been reported depending on the nature of the catalyst. The favoured mechanism in the literature for Pt, Pd, Rh catalysts is the L–H, involving reaction between adsorbed molecules on metal sites, moreover the occurrence of MVK mechanism has been also reported for hydrocarbons oxidation over Pt catalysts. Therefore, it can be concluded that the validity of each mechanism strongly depends on the catalyst (noble metal and nature of the support) as well as on the character of the VOC molecule and it is difficult to generalize.

The addition of promoters, such as Co$_3$O$_4$, CeO$_2$, La^{3+}/Bi^{3+} doped CeO$_2$–ZrO$_2$ oxides, has been successfully applied to increase the activity and thermal stability of Pt, Pd alumina-supported catalysts for VOCs abatement. Catalytic systems composed of noble metals (Pt, Pd) and Ce supported on a metallic structure are efficient for the abatement of CO and VOCs emitted from domestic fireplaces, particularly during ignition and low-charge phases.

Significant progresses have been made in the last years in the development of Pt/TiO$_2$ catalysts effective for complete oxidation even at room temperature of formaldehyde, regarded as the major indoor pollutant in airtight houses.

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